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The University of Chicago.

Founded by JOHN D. ROCKEFELLER.

On Chlorimidoquinones.

A DISSERTATION

SUBMITTED TO THE FACULTIES OF THE GRADUATE
SCHOOLS OF ARTS, LITERATURE, AND SCIENCE,
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY.

DEPARTMENT OF CHEMISTRY.

By LEMUEL CHARLES RAIFORD.

EASTON, PA.:
PRESS OF THE ESCHENBACH PRINTING CO.
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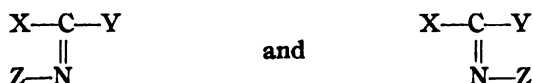
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On Chlorimidoquinones.

In 1890 Hantzsch and Werner¹ formulated the theory that the isomerism of nitrogen compounds of the same composition and structure which contain a doubly bound nitrogen atom is of the same nature as the stereoisomeric ethylene derivatives, like maleic and fumaric acids. In accordance with the theory we should have the two configurations



The objections of Victor Meyer² that the differences between the isomeric benziloximes and dioximes might depend on peculiarities of the hydroxylamine molecule were met by Hantzsch³ by the preparation of stereoisomeric phenylhydrazones of anisylphenylketone; but he was unable to extend⁴ the proof beyond these two closely related groups of compounds, the oximes and the hydrazones, his efforts to prepare stereoisomers in which Z in the above formula is represented by such simple radicals as CH₃, C₆H₅, etc., being un-

¹ Ber. d. chem. Ges., **23**, 11 and 1243 (1890).

² *Ibid.*, **16**, 503 (1883); **21**, 784, 3510 (1888).

³ *Ibid.*, **24**, 3525 (1891).

⁴ Hantzsch: "Stereochemie" p. 141.

successful. The first representatives of such stereoisomers, other than oximes and hydrazones, were prepared in 1903 by Stieglitz and Earle¹ in the form of a pair of stereoisomeric chlorimido esters in which Z in the configuration given is represented by a single chlorine atom. Stieglitz and Hale² prepared a second pair of stereoisomers in 1904, and Hilpert,³ working with Stieglitz in 1907, added five pairs of such compounds to the list. The type is now characterized on a broad and firm basis.⁴

In order to investigate the question of the occurrence of stereoisomeric chlorimides in classes of compounds other than the acid esters, Professor Stieglitz suggested to me to determine whether stereoisomerism can be observed in the case of chlorimidoquinones, comparable with that of the quinone oximes, discussed and investigated by Kehrmann.⁵ Although six chlorimidoquinones whose structure would admit of the occurrence of such stereoisomerism were prepared and studied, and though the structure was varied to cover all the possible types, instances of stereoisomerism were not observed, not even in the case of the chlorimide of 2-chlor-5-methylquinone, whose oxime, according to Kehrmann,⁶ has the most favorable structure for the occurrence and persistence of this form of stereoisomerism. Stieglitz and Hale found that the labile form of stereoisomeric chlorimidonitrobenzoates is very readily converted into the stable form by the action of chlorine and Hilpert confirmed this observation for the chlorimido esters which he studied. Whether the failure to obtain stereoisomeric chlorimidoquinones is due to the fact that chlorine was present in the solution in which the chlorimides were prepared, and that the method of preparation⁷ necessarily involved a much greater time of contact of the reagents with the material than in the case of the preparation of the chlor-

¹ Am. Chem. J., **30**, 399 (1903); **40**, 37 (1908).

² Unpublished reports.

³ Am. Chem. J., **40**, 150 (1908).

⁴ Stereoisomeric chlorimido ketones have recently been prepared by Stieglitz and Peterson.

⁵ Ann. Chem. (Liebig), **279**, 27 (1894); **303**, 1 (1898).

⁶ *Loc. cit.*

⁷ The oxidation of *p*-aminophenols with hypochlorous acid in acid solution.

imido esters, or whether one of the two possible forms is so much the more stable that it is obtained exclusively, it is impossible, of course, to say. It is quite a common experience that cases of stereoisomerism theoretically possible are not readily realizable by our preparation methods.

In the study of the chlorimidoquinones for this work a number of interesting new observations were made on compounds of the phenol and quinone series, and, in particular, some incorrect statements and uncertain points given in the literature on the preparation and structure of such compounds were noted and corrected. All our conclusions were carefully verified by experimental work. In the following paper the most interesting of the observations made are reported.

1. 4-Chlorimido-2-bromquinone

The starting point in the preparation of this compound was 4-nitrophenol, which was first brominated according to the method of Brunk¹ and Körner.² The resulting brom compound was purified by crystallization of its barium salt, from which, by subsequent treatment with hydrochloric acid, the free phenol was obtained. The latter was finally crystallized from water, from which it separated out in colorless needles that melt at 112°.³ It was further identified by the preparation of its reduction products, the corresponding amine and its hydrochloride.

Hydrochloride of 2-Brom-4-aminophenol.—2-Brom-4-nitrophenol was dissolved in the smallest possible quantity of hot alcohol (1 gram to 1 cc.) and to the hot solution was added one-fourth more than the calculated amount of stannous chloride, dissolved in concentrated hydrochloric acid (1 gram to 1 cc.). During this time the flask was shaken and the mixture kept hot in order to prevent the immediate separation of crystals. Next, one volume of concentrated hydrochloric acid was added and the solution set aside to cool. Crystals of the amino hydrochloride soon separated

¹ Z. Chem., 1907, 204.

² *Ibid.*, 1908, 323.

³ The statement of Brunk that 2-brom-4-nitrophenol melts at 102° is probably a misprint. Meldola and Streatfield (J. Chem. Soc., 73, 681 (1898)) prepared this compound by nitrating *o*-bromphenol, and they found 112° as the melting point.

out. These were filtered off and recrystallized as follows: The crude material was dissolved in warm water and the solution filtered through paper, after which one volume of concentrated hydrochloric acid was added to the filtrate. Upon standing, slightly yellowish crystals of the amino hydrochloride, free from tin compounds, were deposited.

The hydrochloride thus obtained is readily soluble in water containing a trace of acid, in alcohol, and in a solution of sodium hydroxide. When heated to 225° the compound begins to blacken, but does not melt. A sample dried *in vacuo* over potassium hydroxide for 72 hours was analyzed for halogen and gave the following results:

0.2913 gram substance gave 0.4311 gram AgHal.

	Calculated for $C_6H_7ONClBr$	Found
Halogen	51.42	51.56

2-Brom-4-aminophenol.—The free amine was easily obtained by treatment of a water solution of the hydrochloride described above with ammonium carbonate solution. The precipitated amine was filtered off at once, and dried on a clay plate. In this condition it melted at 164° and was very nearly pure. The compound is soluble in alcohol, chloroform, ether, and a solution of sodium hydroxide, but much less soluble in benzene. It is best crystallized from the last-named liquid, from which it separates in needles having a faintly brownish color and melting at 165° . Analysis for bromine gave the following figures:

0.2450 gram substance gave 0.2474 gram AgBr.

	Calculated for C_6H_6ONBr	Found
Br	42.54	42.97

4-Chlorimido-2-bromquinone, $O : C_6H_3Br : NCl$.—A portion of the hydrochloride of 2-brom-4-aminophenol, weighing 5 grams, was dissolved in 75 cc. of water to which a trace of hydrochloric acid had been added, and the resulting solution cooled to about 0° . This liquid was then allowed to flow slowly from a tap funnel into acidulated (hydrochloric acid) solu-

tion of sodium hypochlorite¹ which had been cooled to 0°, and in which pieces of ice were floating. The flask containing the hypochlorite was kept surrounded by a mixture of ice and water, and was shaken continuously while the amino hydrochloride was being added. A yellow solid, having the characteristic odor of a chlorimidoquinone, was promptly precipitated, and after standing for a few minutes was filtered off and washed several times with cold water.

When dried on a clay plate the chlorimide began to darken after 24 hours, a change that goes on more rapidly as the temperature rises. The crude product did not have a characteristic melting point, but decomposed suddenly, after softening, when heated above 60°. The compound is soluble in alcohol, ether and chloroform, but less readily so in ligroin. It is best crystallized from the low-boiling (40°–60°) fraction of the latter liquid, because the heat required to saturate the higher boiling fractions to a sufficient degree to give a satisfactory yield of crystals will decompose the chlorimide. Attempts to fractionate² the compound gave negative results. The purest product obtainable decomposed, without melting, when heated to 60°, as already indicated.

For analysis, the method employed by Stieglitz and Earle³ in the determination of halogen in their chlorimido esters, consisting in the liberation of iodine from hydrogen iodide, was first tried; but concordant results could not be obtained, because not only the chlorimide group but the quinone ring, too, oxidizes the hydrogen iodide. Halogen was determined, in this and all other compounds described in this paper, by the Carius method.

0.3460 gram substance gave 0.5233 gram AgHal.

	Calculated for $C_8H_5ONClBr$	Found
Halogen	52.36	52.71

II. 4-Chlorimido-2-chlor-6-bromquinone

This chlorimidoquinone was prepared in accordance with

¹ Graebe: Ber. d. chem. Ges., **35**, 43 and 2753 (1902).

² Hilpert: Loc. cit.

³ Am. Chem. J., **30**, 402 (1903).

the method already described. The starting point was 2-chlor-6-brom-4-nitrophenol, melting at 137° , which was obtained by brominating 2-chlor-4-nitrophenol in glacial acetic acid solution.¹ A portion of this nitro compound was converted into the corresponding amino hydrochloride² by reduction with stannous chloride in the manner already described. By recrystallization of the product colorless plates, that blackened and decomposed without melting when heated above 225° , were obtained. Analysis for halogen gave the following figures:

0.2614 gram substance gave 0.4789 gram AgHal.

	Calculated for $C_6H_6ONCl_2Br$	Found
Halogen	58.27	58.26

*2-Chlor-6-brom-4-aminophenol.*³—The free amine was readily obtained from a water solution of the hydrochloride by precipitation with ammonium carbonate. The mixture was at once filtered and the residue well washed with water, and dried on a clay plate. In this condition the substance is but slightly colored and is otherwise practically pure. It is soluble in alcohol, ether, chloroform, benzene, and a solution of sodium hydroxide. It is best crystallized from benzene, from which it separates in colorless, thin, elongated scales having a melting point of 181° . Analysis for halogen gave the following figures:

0.2411 gram substance gave 0.3606 gram AgHal.

	Calculated for $C_6H_6ONClBr$	Found
Halogen	51.88	52.13

4-Chlorimido-2-chlor-6-bromquinone, $O : C_6H_2BrCl : NCl$.—When a cold solution of the hydrochloride of 2-chlor-6-brom-4-aminophenol was dropped slowly into a cold solution of sodium hypochlorite in the usual way, a yellow solid having the odor characteristic of a chlorimidoquinone was formed.

¹ Ling: J. Chem. Soc., 55, 57 (1889). Clark: Am. Chem. J., 14, 563 (1892).

² Clark (*loc. cit.*) found that this hydrochloride forms a double salt with tin chloride, but he did not isolate the hydrochloride of the amine.

³ This compound is probably identical with Clark's product, though he reports neither melting point nor analysis.

The mixture was filtered, and the solid washed well with cold water and dried on a clay plate. In this condition it melted at 83° – 84° . Attempts to fractionate it gave portions of material having the same melting point. The chlorimide is soluble in alcohol, ether, chloroform and ligroin. After being crystallized from ligroin (70° – 80°), it melted at 87° – 88° , and decomposed suddenly, with charring, when heated to about 175° . The crystals darken after a few days when kept under ordinary conditions. Analysis for halogen gave the results indicated below:

0.2770 gram substance gave 0.5143 gram AgHal.

	Calculated for $C_8H_5ONCl_2Br$	Found
Halogen	59.19	59.02

The study of a dihalogenated chlorimidotoluquinone was next suggested, and an effort was made to obtain this by means of 2,4,6-trichlor-*m*-cresol. It was hoped that this could be nitrated in such a way as to replace by the nitro group the chlorine atom in the para position to the hydroxyl group. In the parallel case of 2,4,6-tribrom-*m*-cresol such substitution takes place very readily, as observed by Claus and Hirsch.¹ No difficulty was experienced in preparing trichlor-*m*-cresol—statements in the literature to the contrary notwithstanding—but it was then found impossible to effect the desired substitution, the trichloride being very much less reactive than the tribromide.

*2,4,6-Trichlor-m-cresol.*²—In a study of the action of chlorine on the cresols, Claus and Schweitzer³ found that *m*-cresol gave a dichlor compound, and that more chlorine could not be introduced. Chandelon⁴ studied the action of chlorinating agents on phenol, and found that treatment of an aqueous solution of phenol with a solution of sodium hypochlorite at 60° – 70° gave trichlorphenol. After repeating Chandelon's work and obtaining the same results, I

¹ J. prakt. Chem., [2] **39**, 61 (1888).

² The trichlortoluenol prepared by Lallemand (Jahresb., **1886**, 620) and reported by Beilstein as trichlorcresol, can hardly be identical with this compound.

³ Ber. d. chem. Ges., **19**, 929 (1886).

⁴ Bull. soc. chim., **38**, 116 (1882).

tried the method with *m*-cresol. An impure product was at first obtained, but the greater portion of it turned out to be the desired compound, 2,4,6-trichlor-*m*-cresol. When the operation was carried out at room temperature instead of 60°–70°, as in the first case, a much better yield of a purer product was secured. This was further purified by distillation in an Anschütz flask. The larger fraction came over at 142°–144° and 14 mm. as an oil which, upon cooling, crystallized out in the form of colorless plates melting at 47°.

Trichlor-*m*-cresol is but slightly soluble in water, but is readily soluble in a solution of sodium hydroxide, from which it is completely precipitated by carbon dioxide. Alcohol, ether, chloroform and ligroin dissolve it easily. Its saturated aqueous solution is not colored violet by ferric chloride. It was analyzed for chlorine and gave the following results:

0.1849 gram substance gave 0.3773 gram AgCl.

	Calculated for $C_7H_5OCl_3$	Found
Cl	50.31	50.40

2,4,6-Trichlor-3-methylphenyl Acetate.—A portion (5 grams) of trichlor-*m*-cresol was mixed with anhydrous sodium acetate and slightly more than the theoretically required amount of acetic anhydride. Action began at once, causing considerable rise of temperature. The flask was warmed until the contents were fluid, and it was then allowed to remain on the electric heater in this condition for about ten minutes. When the solid that formed upon cooling was mixed with water, in order to remove sodium acetate, the acetyl derivative separated out as an oil, which was further washed with water, dried over calcium chloride and distilled. At 273°–274° the chief portion came over as a colorless, viscid liquid of about the consistence of glycerol. The compound was analyzed for chlorine and gave the following figures:

0.2107 gram substance gave 0.3578 gram AgCl.

	Calculated for $C_9H_7O_2Cl_3$	Found
Cl	41.97	42.00

Several attempts were next made to nitrate 2,4,6-trichlor-*m*-cresol. When a glacial acetic acid solution of the compound was mixed with solid sodium nitrite,¹ in accordance with Zincke's method, the unchanged trichlorcresol was recovered from the mixture. Shaking its ethereal solution with silver nitrite also gave negative results. Fuming nitric acid at the room temperature converts it into 2,6-dichlor-toluquinone, along with resinous products.

2,6-Dichlortoluquinone.—Further proof of the structure of 2,4,6-trichlor-*m*-cresol was obtained by oxidizing a portion of it to quinone, which was done by the aid of dichromate mixture. Five grams of trichlor-*m*-cresol was dissolved in 150 cc. glacial acetic acid, and the solution cooled to about 0°, and to this was added gradually the cold dichromate solution. This mixture was allowed to stand for half an hour, after which it was diluted with one volume of water. The yellow solid that formed subsided during an hour, and was then filtered off, washed well with water, and dried on clay plate. A yield of 72 per cent. was obtained.

This quinone is soluble in chloroform, ether, ligroin, and alcohol. Portions crystallized from ligroin and alcohol, respectively, melted at 103°, which agrees with the results obtained by Claus and Schweitzer,² when they oxidized dichlor-*m*-cresol. My product is also probably identical with the dichlortoluquinone prepared by Southworth³ from *m*-cresol, though he states that he could obtain no melting point for his compound, as it began to sublime at 100°. The substance obtained from trichlor-*m*-cresol was shown, both by analysis and by the depression of its melting point when mixed with 4-chlortoluquinone (melting at 105°), not to be an impure sample of the latter. The mixture melted between 85° and 95°. Analysis for chlorine resulted as follows:

0.2242 gram substance gave 0.3380 gram AgCl.

	Calculated for $C_7H_4O_2Cl_2$	Found
Cl	37.14	37.24

¹ J. prakt. Chem., [2] 61, 561 (1900).

² Ber. d. chem. Ges., 19, 931 (1886).

³ Ann. Chem. (Liebig), 166, 270 (1873).

2,6-Dichlortoluhydroquinone.—The dichlortoluquinone (2.5 grams) was mixed with 60 cc. water and the mixture saturated with sulphur dioxide. After standing overnight the mixture was heated to the boiling point, enough water gradually added to dissolve the solid, and then the solution was filtered through paper and set aside to cool. The needle-shaped crystals that formed were collected and dissolved in hot water and the solution saturated with sulphur dioxide. The colorless needles that crystallized out melted at 171° , as found by Claus and Schweitzer,¹ and in close agreement with the results of Southworth.¹

After being dried *in vacuo* over potassium hydroxide for 24 hours the hydroquinone was analyzed for chlorine.

0.3531 gram substance gave 0.5244 gram AgCl.

	Calculated for $C_7H_6O_2Cl_2$	Found
Cl	36.76	36.70

III. 4-Chlorimido-2,6-dibromtoluquinone

The starting point in the preparation of this compound was pure *m*-cresol, obtained by fractionating Kahlbaum's product. From this material 2,4,6-tribrom-*m*-cresol was prepared in accordance with Werner's method.²

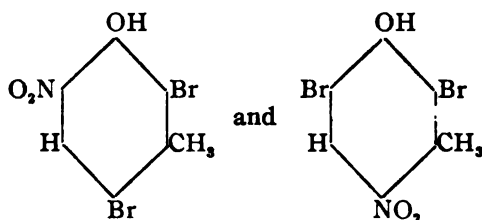
Pure tribrom-*m*-cresol obtained as above specified was next nitrated.³ Thirty grams of the compound was dissolved in 300 cc. glacial acetic acid, the liquid cooled to 12° – 15° and then 10 per cent. more than the calculated quantity of sodium nitrite added during half an hour, while the flask was continually shaken and the temperature kept down to that given above. When the nitrite had all dissolved, the dark liquid was poured with stirring into five volumes of water, and the mixture set aside for some hours to allow the precipitate to subside. At the end of this time the yellow solid was filtered off and dried on a clay plate. A yield of 95 per cent. was obtained. The crude product softened at 65° and

¹ *Loc. cit.*

² Bull. soc. chim., **40**, 275 (1886).

³ Zincke: J. prakt. chem., [2] **01**, 561 (1900).

was completely melted at 113° (when it appeared to decompose), which suggested the possible presence of two compounds.¹ It may be stated at once that isomeric mononitro-dibrom-*m*-cresols, viz.,



were isolated from the mixture.

The best method of separating the compounds present was found to consist in dissolving the dried crude product in hot chloroform (1 gram to 1 cc.) and treating this solution with two volumes of ligroin (40° – 60°). Precipitation of the high-melting isomer (para compound) took place at once. After half an hour this was filtered off and crystallized from benzene, when a compound melting at 128° , with decomposition,² was secured. Repeated crystallization from the same solvent finally gave pale yellow plates melting at 134° with decomposition.³ The substance so obtained has the nitro group in the para position as respects hydroxyl, and is 2,6-dibrom-4-nitro-*m*-cresol. A yield of 35 per cent. was obtained.

When the filtrate from the chloroform-ligroin mixture specified above was allowed to evaporate, it left a yellowish red, sticky mass which, after repeated crystallizations from alcohol, gave deep yellow needles melting at 87° .⁴ This compound is isomeric with the nitro product mentioned above, and was proved (see below) to have the nitro group adjacent to hydroxyl. A yield of 40 per cent. was obtained.

¹ A mixture of the isomers, purified as described in this paper, melts at 79° – 115° with decomposition. Zincke reported the formation of only one isomer, in which the bromine atom para to the hydroxyl group had been replaced.

² Zincke: J. prakt. Chem., [2] 81, 563 (1900).

³ Claus: *Ibid.*, [2] 89, 61 (1888).

⁴ Claus (*loc. cit.*) prepared this compound by brominating 6-nitro-*m*-cresol, and found 93° to be the melting point.

In view of the fact that the melting points found for these compounds did not agree with those given by other workers, both substances were analyzed for halogen and several of their derivatives prepared and studied. Analyses of the nitro compounds for bromine gave the following figures:

- I. The para compound, 2,6-dibrom-4-nitro-*m*-cresol.
0.4668 gram substance gave 0.5662 gram AgBr.

	Calculated for $C_7H_5O_3NBr_2$	Found
Br	51.43	51.26

- II. The ortho compound, 2,4-dibrom-6-nitro-*m*-cresol.
0.4266 gram substance gave 0.5156 gram AgBr.

	Calculated for $C_7H_5O_3NBr_2$	Found
Br	51.43	51.42

Hydrochloride of 2,6-Dibrom-4-amino-m-cresol.—Five grams of the *p*-nitro compound was dissolved in 20 cc. hot alcohol, and to this solution was added stannous chloride dissolved in concentrated hydrochloric acid, as before specified. The hydrochloride obtained upon cooling was recrystallized in the manner already described, and gave colorless needles free from tin compounds. The crystals are readily soluble in water containing a trace of hydrochloric acid, in a solution of sodium hydroxide (giving a liquid that at once becomes brown), and in alcohol, and almost insoluble in chloroform. When heated above 225° the substance blackens but does not melt.

2,6-Dibrom-4-amino-m-cresol.—The free amine was easily prepared from the hydrochloride by treatment of an aqueous solution of the latter with ammonium carbonate. The precipitated base, after being filtered off, washed well with water and dried on a clay plate, melted at 175°–176° with blackening.¹ It is readily soluble in alcohol, benzene, chloroform and a solution of sodium hydroxide, less soluble in ligroin and practically insoluble in water. Portions of the com-

¹ Zincke's statement (J. prakt. Chem., [2] 61, 564 (1900)) that this compound melts at 116° is possibly a misprint, or he had the *o*-amino compound in his hands. He appears to have overlooked the formation of this substance, which melts at 116°, as given below.

pound purified by crystallization from alcohol and by treatment of a chloroform solution with an equal volume of ligroin (40° – 60°), respectively, in both of which cases it separated in colorless crystals, melted at 176° . It was analyzed for nitrogen.

I. 0.4905 gram substance gave 0.0236 gram N (Kjeldahl).

II. 0.4925 gram substance gave 0.0238 gram N.

	Calculated for $C_7H_7ONBr_2$	I	Found	II
N	4.98	4.81		4.83

2,6-Dibrom-4-benzoylamino-m-cresol.—In order to further identify the amine, a portion of it was benzoylated in accordance with the Baumann method, using 2.5 molecules of benzoyl chloride. The product was found to be soluble in alcohol, chloroform and benzene, less soluble in ligroin, and insoluble in water. It was best purified by treatment of its hot chloroform solution with one volume of ligroin (40° – 60°), when colorless crystals melting at 198° were obtained. The pure compound was soluble in a solution of sodium hydroxide and from this hydrochloric acid precipitated the original substance. These results indicated a monobenzoylated product, and they were confirmed by an analysis for nitrogen.

0.4550 gram substance gave 0.0165 gram N (Kjeldahl).

	Calculated for $C_{14}H_{11}O_2NBr_2$	Found
N	3.63	3.62

3,5-Dibrom-6-methyl-p-hydroxyphenylurethane, $HOC_6HBr_2-(CH_3)NHCO_2C_2H_5$.—The first efforts to prepare this compound were made in accordance with Groenvik's¹ method, but the yield was very small and the product could not easily be purified. A much purer substance in satisfactory yield was secured by shaking an alkaline solution of 2,6-dibrom-4-amino-*m*-cresol (obtained by dissolving the amine in a solution of sodium hydroxide) with one molecule of ethyl chlorcarbonate for about ten minutes and, after al-

¹ Bull. soc. chim., **25**, 177 (1876).

lowing the mixture to stand for half an hour, acidifying it with dilute hydrochloric acid. The substance thus obtained was found to be soluble in a solution of sodium hydroxide, from which acids precipitated it in the unchanged form. It was easily purified by mixing with its warm chloroform solution two volumes of ligroin (40°–60°) and removing the brownish solid that was precipitated at once. The urethane melts sharply at 155°, and after being dried for 24 hours *in vacuo* gave the following results when analyzed for nitrogen.

- I. 0.6198 gram substance gave 0.0224 gram N (Kjeldahl).
 II. 0.5752 gram substance gave 0.0217 gram N.

	Calculated for $C_{10}H_{11}O_3NBr_2$	I	Found	II
N	3.96	3.63		3.77

Up to this point the derivatives prepared and analyzed indicate that the amine under consideration has the formula assigned to it. The relative positions of the amino and the hydroxyl groups were determined by the behavior of the compound when oxidized with the usual dichromate mixture, in which case it gave a quinone melting at 117°, and evidently identical with the 2,6-dibromtoluquinone that Claus and Dreher¹ obtained by oxidizing 2,4,6-tribrom-*m*-cresol. In order to decide this a portion of the tribrom-*m*-cresol used in the preparation of the compounds described above was oxidized to quinone in accordance with the directions given by Claus. A compound having a melting point of 117°, which was not depressed when mixed with the quinone obtained directly from the amine, resulted.

4-Chlorimido-2,6-dibromtoluquinone, $O : C_6HBr_2(CH_2) : NCl$.
 —When a cold solution of the hydrochloride of 2,6-dibrom-4-amino-*m*-cresol was oxidized in the usual way with an acidified solution of sodium hypochlorite, an immediate precipitate of chlorimidoquinone was formed. This was filtered off

¹ J. prakt. Chem., [2] **39**, 370 (1889). Claus and Dreher found that this dibromtoluquinone melts at 115°. Claus and Hirsch (*Ibid.*, p. 60) report 117° as the melting point of the corresponding hydroquinone; but this is probably an error, since hydroquinones usually melt much higher than their quinones. Reduction of our dibromtoluquinone with sulphur dioxide in the usual way gave a hydroquinone that crystallized from water in colorless crystals and had a constant melting point of 150°.

and washed with water, and when dried on a clay plate it melted at 85°–86°. A yield of 85 per cent. was obtained. The compound is readily soluble in alcohol, chloroform, and ligroin, but insoluble in water. Attempts to fractionate the substance in accordance with the methods indicated above gave crystals having the same melting point, 86°. The best method of purification of the chlorimide is crystallization from ligroin (40°–60°), from which it separates in yellow hexagonal plates melting at 86°, and having the characteristic odor of this class of substances. Determination of nitrogen resulted as follows:

- I. 0.5990 gram substance gave 0.0263 gram N (Kjeldahl).
- II. 0.7515 gram substance gave 0.0334 gram N.

	Calculated for $C_7H_4ONClBr_2$	Found	
N	4.46	4.39	4.44

It has been noted (p. 13) that the nitration of 2,4,6-tri-brom-*m*-cresol under the conditions described in this paper gives rise to two isomeric mononitro derivatives, one of which (melting at 134° with decomposition) has been shown to have the nitro group para to hydroxyl. When this had been done it was at once suspected that the other one (melting at 87°) had the nitro group ortho to hydroxyl. The behavior of its derivatives described below shows that this is the case.

Hydrochloride of 2,4-Dibrom-6-amino-m-cresol.—Five grams of 2,4-dibrom-6-nitro-*m*-cresol was dissolved in 50 cc. hot alcohol and then reduced with stannous chloride in the usual way. It was noted that the hydrochloride obtained is much less readily soluble in water than is its isomer, the para compound, and could not be purified in exactly the manner employed with the latter. Two modifications were tried, viz., crystallization from alcohol and treatment of the alcoholic solution with concentrated hydrochloric acid. In both cases the crystals secured were free from tin compounds. Exactly as in the case of the para compound, this hydrochloride is but sparingly soluble in chloroform, but is readily soluble

in a solution of sodium hydroxide, forming a brown liquid. Nitrogen determinations gave the following figures:

- I. 0.6942 gram substance gave 0.0292 gram N (Kjeldahl).
- II. 0.5553 gram substance gave 0.0239 gram N.

	Calculated for $C_7H_5ONClBr_2$	I	Found	II
N	4.41	4.20		4.30

2,4-Dibrom-6-amino-m-cresol.—A solution of the hydrochloride in very dilute hydrochloric acid was mixed with a slight excess of a solution of ammonium carbonate, and the precipitated amine at once filtered off and washed well with water. When dry the base was further purified by treatment of its warm chloroform solution with two volumes ligroin (40° – 60°), from which it crystallized in brownish scales melting at 116° – 117° .¹ Alcohol, chloroform and solutions of sodium hydroxide dissolve the amine easily, giving in the latter case a strongly colored liquid. Nitrogen analyses gave the results recorded below:

- I. 0.6323 gram substance gave 0.0326 gram N (Kjeldahl).
- II. 0.6683 gram substance gave 0.0342 gram N.

	Calculated for $C_7H_7ONBr_2$	I	Found	II
N	4.98	5.15		5.11

2,4-Dibrom-3-methyl-6-benzoylamino-phenyl Benzoate.—The amine just described was further identified by treatment with benzoyl chloride by the Baumann method, 2.5 molecules of benzoyl chloride being used. The product was collected on a filter, dried on a clay plate, and repeatedly crystallized from alcohol until it was practically colorless and melted sharply at 188° . The compound is easily soluble in chloroform and ether, less readily so in ligroin, and insoluble in solutions of sodium hydroxide. It was regarded as the dibenzoylated compound, and analysis for nitrogen agreed with this view:

¹ It will be noted that Zincke (J. prakt. Chem., [2] 61, 564 (1900)) found 116° as the melting point of the para compound, while I found 176° for the compound that I proved to be the para product.

- I. 0.5070 gram substance gave 0.0156 gram N (Kjeldahl).
 II. 0.5070 gram substance gave 0.0159 gram N.

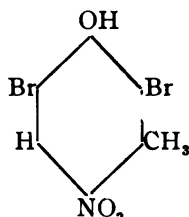
	Calculated for $C_{21}H_{18}O_3NBr_2$	I	Found	II.
N	2.86	3.07		3.13

3,5-Dibrom-4-methyl-o-hydroxyphenylurethane, $HOC_6H(CH_3)-Br_2NHCO_2C_2H_5$.—As in the case of the para compound, an attempt was made to prepare this urethane by Groen-vik's method,¹ but the very small yield, taken in connection with the difficulty experienced in obtaining a pure product, made it advisable to try some other method. A yield of 60 per cent. was obtained by shaking an alkaline solution of the corresponding aminocresol with one molecule, of ethyl chlorcarbonate, and the product was not difficult to purify. It was crystallized by mixing with its warm chloroform solution an equal volume of ligroin ($40^\circ-60^\circ$). The crystals that separated were brownish and readily soluble in alcohol and in solutions of sodium hydroxide, from which liquid they were separated unchanged by the addition of acid. They melted sharply at 169° . A portion of the compound dried in vacuo for 24 hours was analyzed for nitrogen.

- I. 0.6776 gram substance gave 0.0271 gram N (Kjeldahl).
 II. 0.5376 gram substance gave 0.0201 gram N.

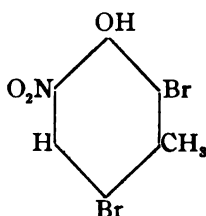
	Calculated for $C_{10}H_{11}O_3NBr_2$	I	Found	II
N	3.96	3.99		3.73

The preparation and analyses of the derivatives of the dibromnitro-m-cresol now under consideration indicate that it is isomeric with the one already disposed of, and which was shown to have the structure



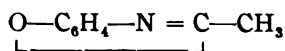
¹ Bull. soc. chim., 25 177 (1876).

by the ease with which it was ultimately converted into the corresponding quinone. Direct proof that the substance now in question has the nitro group adjacent to hydroxyl, and has the structure



was secured as follows:

In a study of the behavior of aminophenols, Ladenburg¹ found that he could distinguish between the ortho and para varieties by the difference in reaction of the two compounds toward acetic anhydride. The ortho compounds give condensation products which he called ethenylaminophenols, or anhydro bases,



while the para compounds give diacetyl derivatives,



This method was tried on the aminocresol obtained from the nitro compound now being studied.

2,4-Dibrom-3-methyl-6-acetylaminophenol Acetate. — Three grams of the corresponding dibromamino-*m*-cresol was mixed with acetic anhydride (2 mol.) as above indicated. Interaction began immediately with the evolution of heat. The flask was next attached to a reflux condenser and warmed gently until the mass became liquid, after which it was boiled for two hours. Upon cooling, a solid that melted at 207° was formed. Repeated crystallization from alcohol gave long, colorless, silky needles melting sharply at 216°, soluble in chloroform and ligroin, but insoluble in solutions of sodium hydroxide except on standing. The behavior toward alkali

¹ Ber. d. chem. Ges., 9, 1524 (1876).

pointed to a diacetyl derivative, and this indication was confirmed by analyses for nitrogen and bromine.

- I. 0.4134 gram substance gave 0.0165 gram N (Kjeldahl).
 0.2382 gram substance gave 0.2466 gram AgBr.
 II. 0.3711 gram substance gave 0.0144 gram N.

	Calculated for $C_{11}H_{11}O_2NBr_2$	I	Found II
N	3.83	3.99	3.88
Br	43.82	44.08

That the base is nevertheless an *o*-aminophenol derivative is shown conclusively by the following determination. In a study of the rearrangements of *o*-aminophenylethyl carbonate, Ransom,¹ working with Stieglitz, showed that when its hydrochloride is dissolved in water it goes over into *o*-hydroxyphenylurethane. Upson,² also working with Stieglitz, studied this rearrangement in quite a number of substances, and found that while it is a general reaction for ortho compounds it does not take place with the corresponding para compounds. With these facts in view, the dibromnitro-*m*-cresol (melting at 87°) in question was converted into its carbonate, and this was reduced to the amino hydrochloride, and the latter then allowed to react with water in the usual way. Its behavior showed conclusively that the dibromnitro-*m*-cresol (melting at 87°) is an *o*-nitrophenol, and that its reduction product is an *o*-aminophenol.

2,4-Dibrom-3-methyl-6-nitrophenylethyl Carbonate, $O_2NC_6H_3Br_2(CH_3)OCO_2C_2H_5$.—Six grams of 2,4-dibrom-6-nitro-*m*-cresol was dissolved in 300 cc. water containing slightly more than the theoretically required amount of sodium hydroxide, and to this was added 1.25 molecules of ethyl chlorcarbonate, after which the mixture was shaken for twenty to thirty minutes, or until the red color characteristic of the sodium salt of the nitrocresol had disappeared. A yellow oil, that solidified on cooling, separated out, and after standing for some time was filtered and dried. The substance is very soluble in alcohol, ether, chloroform, ligroin and glacial acetic acid, and

¹ Am. Chem. J., **22**, 43 (1900).

² *Ibid.*, **32**, 13 (1904).

could not be crystallized from any of these liquids. The purest sample secured was obtained by pouring the glacial acetic acid solution into water. The oil that separated solidified on standing, and was then filtered off and dried. It melted at 43° – 45° .

The nitrocarbonate was next reduced¹ by shaking its glacial acetic acid solution with tin² and concentrated hydrochloric acid until the liquid was practically colorless, after which it was filtered through paper and the filtrate mixed with two volumes of water and then allowed to stand overnight in order to enable the phenolcarbonate to rearrange and form the corresponding urethane by a migration of the carbonate group from the phenol group to the amine group.³ The solid that formed was collected on a filter and dried on a clay plate. In this condition it melted at 167° – 169° . It was further purified by solution in warm chloroform and treatment of this solution with one volume of ligroin (60° – 80°). The crystals so obtained melted sharply at 169° , which is the melting point of 3,5-dibrom-4-methyl-*o*-hydroxyphenylurethane already described (p. 19). A mixture of these two products has the same melting point as either of them separately, from which it follows that they are identical, and that in the dibromnitro-*m*-cresol in question the hydroxyl and the nitro groups are adjacent to each other. It will be noted that this method of proving the relative positions of the hydroxyl and nitro (amino) groups by means of rearrangement is easier of execution and gives more conclusive evidence than does Ladenburg's method.

IV. The Three Chlorimidochlortoluquinones

In their proof of the structure of the stereoisomeric oximes obtained from 4-chlortoluquinone, Kehrmann and Tichvinsky⁴ found that reduction of the oximes by means of stannous chloride gave a chloraminocresol that is identical with the base they obtained when they reduced the product secured

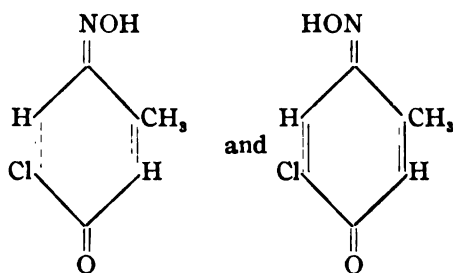
¹ Ransom: *Am. Chem. J.*, **33**, 14 (1900).

² Equally satisfactory results were obtained by the use of zinc.

³ Ransom: *Loc. cit.*

⁴ *Ann. Chem. (Liebig)*, **303**, 20 (1898).

by chlorinating 6-nitro-*m*-cresol in glacial acetic acid solution. In the latter reaction Kehrman¹ assumed that chlorine took a position para to methyl, and from such a view assigned to the oximes the stereoisomeric formulas



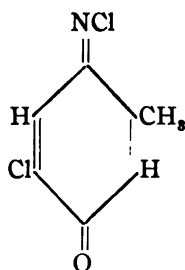
He states that this is the structure most favorable to the occurrence and persistence of this form of stereoisomerism. My experiments in the attempts to prepare the stereoisomeric chlorimidoquinones corresponding to these oximes involved the preparation of a chloraminocresol from 6-nitro-*m*-cresol, and it was found to have a melting point of 166°–167°, which is different from that (204°–205°) given by Kehrman, a fact that at once made necessary a repetition of Kehrman's work on the oximes. The latter were prepared (the stereoisomers were not separated) and reduced according to the directions given, and the resulting hydrochloride of the chloraminocresol decomposed by ammonium carbonate in the usual way. The base obtained melted at 206°–207°, which is in close agreement with the observation of Kehrman. The acetyl derivative, the quinone and the hydroquinone obtained from this base also had the properties reported by Kehrman and others² in the literature. It was further identified by the preparation of its dibenzoate (p. 30).

When the chloraminocresol (melting at 206°–207°) was oxidized to the chlorimidoquinone it gave a product melting at 91°, while the chloraminocresol (melting at 166°–167°)

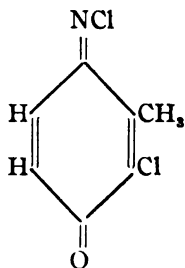
¹ *Loc. cit.*

² Schniter's statement (Ber. d. chem. Ges., 20, 2286 (1887)) that the monochlorinated toluquinone, melting at 105°, could not be obtained free from the higher chlorinated products is not confirmed by the analysis reported by him. The calculated percentage of chlorine given by him is incorrect.

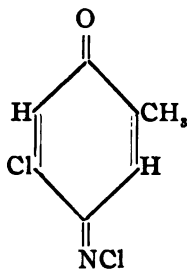
obtained from the chlorine derivative of *p*-nitro-*m*-cresol gave a chlorimidoquinone melting at 87° . A mixture of the two chlorimides melts at 65° – 70° , which shows that they are not identical. If Kehrmann's assumptions as to the structure of the chlornitro-*m*-cresol formed by chlorinating *p*-nitro-*m*-cresol were correct, the two chlorimides would have the same structure and would therefore be stereoisomers of the type sought by us. However, the low melting point obtained by me for the chloraminocresol prepared by way of chlornitro-*m*-cresol, as compared with the melting point (204° – 205°) given by Kehrmann for the chloraminocresol obtained by reduction of his oximes (and confirmed by me) suggested plainly that the two chlorimides, as well as the two amino products, might well be structural isomers rather than stereoisomers. By subsequent investigation I was able to prove that the chlorimides are indeed structural isomers—the chlorimide, melting at 91° , obtained from Kehrmann's chloraminocresol having the structure of 6-chlorimido-4-chlortoluquinone,



while that obtained from the chloraminocresol, melting at 166° – 167° , derived from *p*-nitro-*m*-cresol is 6-chlorimido-2-chlortoluquinone,



melting at 87°. A third chlorimidochlortoluquinone, melting at 65°, was obtained from 2-methyl-4-amino-5-chlor-*o*-cresol (from *m*-nitro-*p*-chlortoluene) and has the structure of 4-chlorimido-2 methyl-5-chlorquinone,

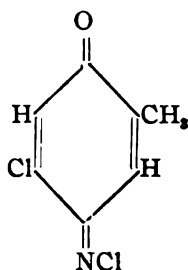


6-Chlorimido-4-chlortoluquinone.—It is possible that when Kehrman chlorinated *p*-nitro-*m*-cresol, the chlorine, to a certain extent at least, entered the position para to the methyl group, in the way he assumed (Kehrman did not isolate the chloride); but when I carried out the chlorination of the same substance, following Kehrman's directions as closely as the brief descriptions will permit, except that I isolated and purified all my products, the chlorine, as proved below, must have persistently entered chiefly into the position ortho to the methyl group, that is, between it and the hydroxyl group. It seems possible, now that I have cleared up the facts, that in both cases a mixture of both chlorides is formed—the proportions varying according to conditions that have not yet been determined; and that Kehrman obtained derivatives (amine, etc.) of one compound, while I secured those of another. It is beyond question, however, that the derivative which I isolated is always formed under the conditions followed by me. In a very closely related case, the chlorination of *o*-nitrotoluene, I was able to establish conclusively (see below) the formation of the two chlorine derivatives, containing chlorine ortho and para to the methyl group, although Janson¹ had reported the formation of but one (in this case the ortho compound).

¹ Centralb., 1900, I, 1110.

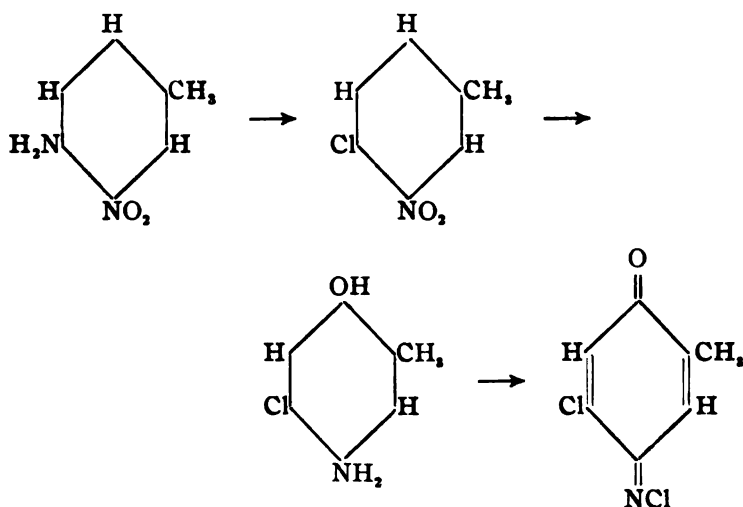
The proof of the structural isomerism of the three chlorimidochlortoluquinones, melting at 91° , 87° , and 65° , respectively, consisted in showing first that not only do the three chlorimides depress each others' melting points, but that all their derivatives—their reduction products, the corresponding aminophenols and their acyl derivatives, the quinones obtained by the oxidation of the aminophenols, and the hydroquinones obtained by the reduction of the quinones—form different series with different melting points and other properties. If the difference were due to space relations of the :NCl group, this difference would vanish with reduction of the group, and identical compounds would result. In the second place, the structure of each of the three chlorimides was brought into definite relations with simpler derivatives of known or readily proved structure.

The chlorimidochlortoluquinone whose melting point is 65° was brought into relation with 3-nitro-4-chlortoluene, and found to have the structure



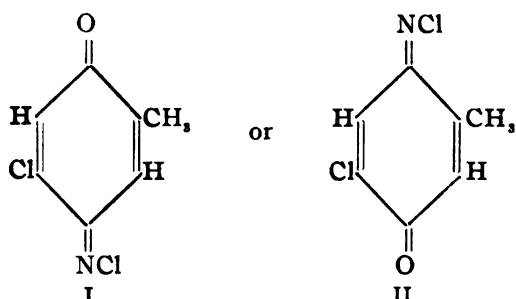
This connection was established by converting *m*-nitro-*p*-toluidine into *m*-nitro-*p*-chlortoluene by the Sandmeyer reaction, transforming this *m*-nitro-*p*-chlortoluene into the corresponding chloraminocresol (melting at 197° – 199° with blackening) by electrolytic reduction and rearrangement in concentrated sulphuric acid solution by Gattermann's method,¹ and by converting this chloraminocresol directly into the chlorimide (melting at 65°). The steps may be summarized as follows:

¹ Gattermann and Kaiser: Ber. d. chem. Ges., 18, 2599 (1895).

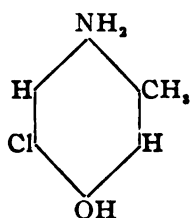


The chlorimidochlortoluquinone that melts at 91° was obtained by the action of hypochlorous acid on the reduction product of Kehrman's oximes; the oximes in turn were obtained by Kehrman from so-called *p*-chlortoluquinone in which the chlorine is assumed to be in the para¹ position to the methyl group. The direct proof that such is the case was brought by the oxidation of 4-chlor-3-amino-6-hydroxytoluene, prepared as just described. The same chlortoluquinone (melting at 105°) as that used by Kehrman in the preparation of his oximes was obtained. The para position of the chlorine atom being thus established, the chlorimide melting at 91° must have the structure

¹ That position for chlorine was generally assumed in the chlortoluquinone from which Kehrman started, but we can find no direct proof for the assumption. The chlortoluquinone is obtained by oxidation of chlortoluhydroquinone which, in turn, is obtained by the action of hydrochloric acid on toluquinone, in accordance with Schniter's (Ber. d. chem. Ges., **20**, 2286 (1887)) reaction. By the corresponding action of hydrobromic acid on toluquinone, Kehrman and Rust (Ann. Chem. (Liebig): **303**, 24 (1898)), obtained a bromtoluquinone melting at 105° , and evidently identical with the compound (melting at 106°) in which Gattermann (Ber. d. chem. Ges., **27**, 1931 (1894)) proved definitely that bromine goes into a position para to methyl. But Schniter (Ber. d. chem. Ges., **20**, 1317 (1887)) has shown by his work on thymoquinones that the position taken by chlorine in his reaction is sometimes *not* the same as that taken by bromine.

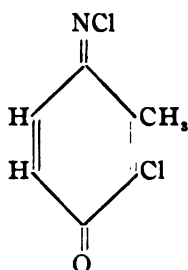


But structure (I) has just been proved to be that of the chlorimide melting at 65° , obtained from the chloraminocresol melting at 197° – 199° , which cannot possibly be stereoisomeric, but must be structurally isomeric, with the chloraminocresol that melts at 206° – 207° , and which was obtained by the reduction of the chlorimide melting at 91° . The latter, therefore, cannot be stereoisomeric, but must be structurally isomeric, with the chlorimide melting at 65° , and must have structure (II), and its chloraminocresol (melting at 206° – 207°) must be 4-chlor-6-amino-3-hydroxytoluene,

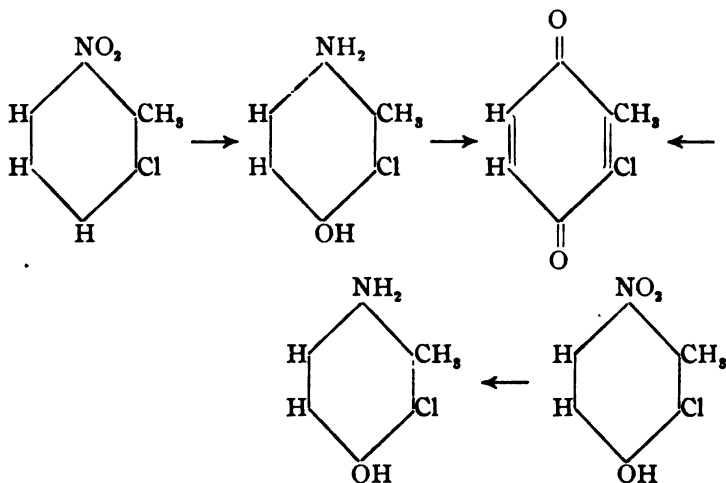


This, it may be added, brings proof, also, of the correctness of the structure assigned by Kehrman to his stereoisomeric oximes and their derivatives. His own proof, in the light of the above, does not appear unassailable.

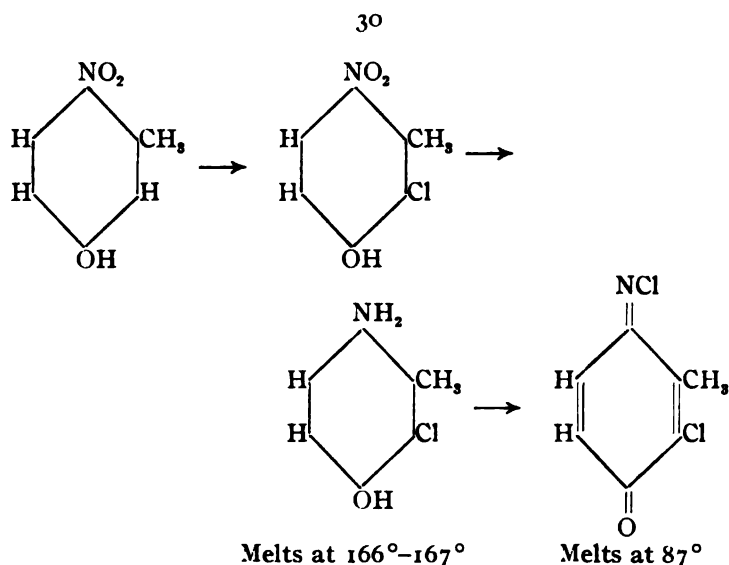
The third chlorimidochlortoluquinone (melting at 87°), first obtained from the chlorination product of *p*-nitro-*m*-cresol, has the structure



The chlortoluquinone obtained by oxidation of its reduction product, chloraminocresol (melting at 166° – 167°), was brought by me into relationship with *o*-chlor-*o*-nitrotoluene. This was converted into the corresponding aminocresol by electrolytic reduction in sulphuric acid solution, and from this was obtained, by oxidation, the same chlortoluquinone (melting at 55°) as from the chloraminocresol melting at 166° – 167° . The changes are indicated as follows:



In this way the position of the chlorine atom in the chlorimide and its derivatives is established. The position of the chlorimide group is determined by the preparation of the chlorimide from *p*-nitro-*m*-cresol:



The experimental data on which these conclusions are based will now be given:

2-Chlor-4-benzoylamino-5-methylphenyl Benzoate.—This compound was prepared as a further simple derivative to identify Kehrman's aminocresol, melting at 206°-207°. A portion of the amine was dissolved in a solution of sodium hydroxide, and this was shaken with benzoyl chloride (3 mol.) until the odor of the chloride had about disappeared. The solid that separated was filtered off and repeatedly crystallized from alcohol until it was nearly colorless. It melts at 220°. The substance was found to be soluble in chloroform and ether, but insoluble in a solution of sodium hydroxide. This fact and the figures given on analysis indicate a dibenzoylated compound:

- I. 0.5562 gram substance gave 0.0195 gram N (Kjeldahl).
- II. 0.3400 gram substance gave 0.0124 gram N.

	Calculated for $C_{27}H_{16}O_3NCl$	I	Found	II
N	3.83	3.50		3.63

³
 6 - Chlorimido - 4 - chlortoluquinone, O : C₆H₂Cl(CH₃) : NCl.—
 Five grams of the hydrochloride of the aminocresol obtained

by reduction of Kehrman's oximes was dissolved in 100 cc. water to which a trace of hydrochloric acid had been added, and the solution cooled to about 0° and then dropped slowly into a cold acidified solution of sodium hypochlorite. The yellow solid that formed was filtered off, washed with cold water and dried. The crude product melted at 88° , and attempts to fractionate it gave lots of crystals having the same melting point, 91° . It is readily soluble in alcohol, chloroform and ligroin, from which latter it is best crystallized, separating in the form of needles radiating from a common center. A warm alcoholic solution of the compound was easily reduced by stannous chloride dissolved in concentrated hydrochloric acid, with the formation of the corresponding chloraminocresol.

The chlorimide was analyzed for chlorine and for nitrogen and gave the following results:

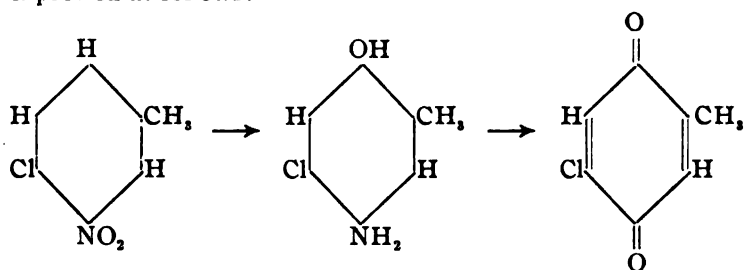
- I. 0.2067 gram substance gave 0.3120 gram AgCl.
0.4753 gram substance gave 0.0336 gram N (Kjeldahl).
- II. 0.2107 gram substance gave 0.3192 gram AgCl.
0.5351 gram substance gave 0.0376 gram N.

	Calculated for $C_7H_5ONCl_2$	I	Found II
Cl	37.32	37.32	37.45
N	7.37	7.06	7.03

Proof of the Structure of p-Chlortoluquinone.—For the proof of the structure of the chlortoluquinone which Kehrman employed in the preparation of his stereoisomeric oximes, and, at the same time, the determination of the position of chlorine in the chlorimide that has just been described, a quantity of pure 3-nitro-4-chlortoluene¹ was first prepared by the Sandmeyer reaction from 3-nitro-4-toluidine, and then reduced electrolytically to an aminocresol by Gattermann's method. For the latter purpose 10 grams of the pure oil was dissolved in 100 grams of sulphuric acid (1.84), and to this solution 0.5 cc. water was added. The liquid so obtained was poured into a porous cup, and the latter placed in a beaker of convenient size so that the distance between the outer

¹ Gattermann and Kaiser: Ber. d. Chem. Ges., 18, 2599 (1885).

wall of the porous cup and the inner wall of the beaker was about 1.5 cm. Outside the porous cup was placed a mixture of 100 grams of sulphuric acid (1.84) and 5 grams of water. The cathode was placed in the liquid in the porous cup and a current of 7.5 volts and 1.9 to 2.1 amperes was passed for 15 hours. The liquid was then allowed to cool and was poured into six volumes of water. Slight precipitation¹ took place at once, and the mixture stood until it had reached the room temperature and the supernatant liquid was clear. This was next filtered off, and the filtrate, which was deep blue in color, was neutralized with a solution of sodium carbonate. The chloraminocresol formed was precipitated. After filtration the residue was washed with water, and, without further purification, was at once dissolved in very dilute hydrochloric acid, cooled and mixed with a solution of ferric chloride. When the mixture so obtained was distilled with steam, a quinone melting at 105°, and identical with that obtained by oxidizing Kehrman's chloraminocresol (melting at 206°–207°), passed over. A mixture of the two substances melts at the same temperature as either of them separately. A yield of 60 per cent. was obtained. The reactions may be expressed as follows:



3-Chlorimido-4-chlortoluquinone (melting at 65°),

⁶O : C₆H₂Cl(CH₃) : ³NCl.—A second portion of the chloraminocresol, obtained from 3-nitro-4-chlortoluene by electrolytic

¹ This precipitate is probably a sulphonic acid. Gattermann found that with *o*-nitrotoluene the chief product was a sulphonic acid of the corresponding aminocresol. Noyes and Clement (Ber. d. chem. Ges., **26**, 991 (1893)) found that the sulphonic acid was not formed when they used sulphuric acid below a certain concentration. In my work some sulphonic acid appeared to form in every case, the amount being smaller when halogen was in the ring.

reduction, was dissolved in dilute hydrochloric acid and the solution cooled to about 0° and then dropped slowly into a cold acidified solution of sodium hypochlorite in the usual way. A chlorimidoquinone, having the characteristic odor, and mixed with some resinous products, was precipitated. It was collected on a filter, washed with cold water and dried. Attempts to fractionate gave portions of solid all having the same melting point, 65° . The compound is soluble in alcohol, ether, and chloroform, but is best crystallized from ligroin, from which it separates in brownish wartlike nodules. Analysis for chlorine indicates that it has the same composition as, and is isomeric with, 6-chlorimido-4-chlortoluquinone, melting at 91° , described above.

0.1965 gram substance gave 0.2969 gram AgCl.

	Calculated for $C_7H_5ONCl_2$	Found
Cl	37.32	37.35

6-Chlorimido-2-chlortoluquinone (melting at 87°),

$O : C_6H_2Cl(CH_3) : NCl$.—The starting point in the preparation of this compound was *m*-cresol, which was obtained by fractionating Kahlbaum's pure product. Fifty grams of the liquid boiling at 199° – 200° (uncorr.) was nitrated in accordance with the method of Staedel and Kolb,¹ and the isomeric nitro products that resulted were separated by distillation with steam. The para compound, which is not volatile under these conditions, and which was obtained in crude form from the distillation residue, was further purified by successive crystallization of its sodium salt from water. These crystals were then decomposed by treatment of their aqueous solution with dilute sulphuric acid, and the free nitrocresol subsequently crystallized from hot water, from which it separated in very nearly colorless needles melting at 127° – 129° . A yield of 38 to 40 per cent. was obtained.

2-Chlor-6-nitro-*m*-cresol, $HO.C_6H_2Cl(CH_3)NO_2$.—Ten grams of purified 6-nitro-*m*-cresol was chlorinated,² the operation

¹ Ann. Chem. (Liebig), **259**, 210 (1890).

² *Ibid.*, **303**, 23 (1898).

being started at the room temperature, and the reaction mixture was poured with stirring into six volumes of water. A colorless solid precipitated out at once, and was filtered off and dried on a clay plate. The substance is soluble in benzene, ligroin and chloroform, very soluble in alcohol, and but very slightly soluble in water. After being crystallized twice from benzene it melted sharply at 133° , and this was not changed when a portion of the material was crystallized in the form of its sodium salt, this decomposed by acid, and the free cresol again crystallized from benzene. Analyses¹ for chlorine and for nitrogen gave the following results:

0.2302 gram substance gave 0.1784 gram AgCl.

0.1881 gram substance gave 12.25 cc. N at 21° and 752.5 mm. (uncorr.).

	Calculated for $C_7H_6O_2NCl$	Found
Cl	18.90	19.15
N	7.46	7.34

Hydrochloride of 2-Chlor-6-amino-m-cresol.—Five grams of 2-chlor-6-nitro-*m*-cresol was dissolved in hot alcohol and reduced with stannous chloride in the manner already described, forming practically colorless crystals that darkened when heated above 225° , but did not melt when heated as high as 250° . The crystals are readily soluble in water acidulated with hydrochloric acid, in alcohol and in a solution of sodium hydroxide with the formation of a brown liquid. A sample dried *in vacuo* for 72 hours over potassium hydroxide gave the following results when analyzed for chlorine:

0.2674 gram substance gave 0.3966 gram AgCl.

	Calculated for $C_7H_6ONCl_2$	Found
Cl	36.54	36.66

2-Chlor-6-amino-m-cresol, $HO.C_6H_2Cl(CH_3)NH_2$.—The free base was easily obtained by treatment of an aqueous solution of the hydrochloride with ammonium carbonate. The precipitate was collected on a filter at once, washed with water

¹ Kehrman (loc. cit.) reports no analyses for the intermediate products through which he obtained proof of the structure of his oximes.

and dried. In this condition the compound was nearly pure, as was shown by the fact that crystallization did not change the melting point. It dissolves in alcohol, benzene, chloroform and solutions of sodium hydroxide, but much less readily in ligroin. Portions were obtained in practically colorless crystals by crystallizing from 75 per cent. alcohol. These melted at 166° – 167° , with slight darkening. That this substance could not be an impure specimen of the compound obtained by reducing Kehrman's oximes was shown by the fact that a mixture of the two melts lower than either of them separately, viz., 157° , as well as by the fact that the derivatives now to be described are not identical with the corresponding compounds obtained from the amine secured by the reduction of the oximes. Analysis for chlorine gave the following results:

0.2982 gram substance gave 0.2716 gram AgCl.

	Calculated for C_7H_9ONCl	Found
Cl	22.50	22.51

4-Acetylamino-5-methyl-6-chlorophenyl Acetate.—In order to further identify this aminocresol, it was converted into an acetyl derivative by warming it with anhydrous sodium acetate and acetic anhydride (1.5 mol.). After recrystallization from benzene, long, colorless, silky needles melting at 178° were secured. A mixture of this substance with the diacetyl derivative (melting at 162°) obtained from 4-chlor-6-amino-*m*-cresol melts at 140° – 149° . The new compound did not dissolve in solutions of sodium hydroxide, and this behavior, taken in connection with the percentage of chlorine found upon analysis, indicated a diacetyl derivative:

0.2711 gram substance gave 0.1618 gram AgCl.

	Calculated for $C_{11}H_{12}O_2NCl$	Found
Cl	14.67	14.75

2-Chlortoluquinone, $\overset{3}{O} : C_6H_2\overset{2}{Cl}\overset{1}{CH_3} : \overset{6}{O}$.—The new chloraminocresol was further characterized by conversion of a portion of it into its quinone by treatment with a cold dichromate

mixture. After standing, the precipitate that formed was collected on a filter and dried. A yield of 60 per cent. was obtained. A more convenient method is to mix the cold, slightly acid solution of the hydrochloride of the amine with a solution of ferric chloride, and then to distil the quinone with steam. The quinone is appreciably soluble in water, and is very readily soluble in alcohol, chloroform and ligroin. Crystals deposited from a solution in the latter solvent melted at 55° , and a mixture of the substance with 4-chlortoluquinone, employed by Kehrman in the preparation of his stereoisomeric oximes, melts at 46° , which shows that the compound in question is a new one. It completes the list of possible chlortoluquinones, the other two being already known, viz., *p*-chlortoluquinone, melting at 105° , prepared by Schniter,¹ and *m*-chlortoluquinone, melting at 90° , prepared by Claus and Schweitzer.² The syntheses (see below) and analysis for chlorine indicate that this compound is isomeric with the substance Kehrman used as a starting point:

0.2830 gram substance gave 0.2611 gram AgCl.

	Calculated for $C_7H_5O_2Cl$	Found
Cl	22.65	22.79

2-Chlortoluhydroquinone, $\overset{3}{HOC_6H_2}\overset{2}{Cl}(\overset{1}{CH_3})\overset{6}{OH}$.—A portion of 2-chlortoluquinone was mixed with water and the mixture saturated with sulphur dioxide. The yellow color of the quinone was discharged, and after standing overnight in a cool place the solid was nearly colorless. This was filtered off and repeatedly recrystallized from hot water, the filtered solution in each case being decolorized by sulphur dioxide. Short, colorless leaflets melting at 173° , that colored slightly when exposed to the air, crystallized out. These were found to be soluble in alcohol but much less so in chloroform, ligroin, and benzene. In solutions of sodium hydroxide they dissolve, giving first a green color that rapidly changes to a dark red. A mixture of this compound with 4-chlortoluhydro-

¹ Ber. d. chem. Ges., **20**, 2286 (1887).

² J. prakt. Chem., [2] **38**, 328 (1888).

quinone, melting at 176°, melts at 146°–158°, which shows that they are not identical. Analysis for chlorine indicates that they are isomeric.

0.3205 gram substance gave 0.2895 gram AgCl.

	Calculated for $C_7H_7O_2Cl$	Found
Cl	22.36	22.33

6-Chlorimido-2-chlortoluquinone, $\overset{3}{O} : C_6H_2\overset{2}{Cl}(\overset{1}{CH_3}) : \overset{6}{N}Cl$. — A portion of the new chloramino-*m*-cresol, melting at 166°–167°, was dissolved in very dilute solution of hydrochloric acid, and this liquid was cooled to about 0° and then dropped slowly into a cold acidified solution of sodium hypochlorite in the usual way. A yellow solid, having the odor characteristic of a chlorimidoquinone, separated out at once. This was filtered off, washed with cold water, and dried on a clay plate. It melted at 86°–87°. All lots of crystals obtained in attempts to fractionate it had the same melting point, 87°. A mixture of this compound with 6-chlorimido-4-chlortoluquinone, melting at 91° (obtained from the chloraminocresol that resulted from the reduction of Kehrmann's oximes), melts at 60°–65°. Analyses for chlorine and for nitrogen gave the following results:

- I. 0.1671 gram substance gave 0.2536 gram AgCl.
0.2050 gram substance gave 0.0146 gram N (Kjeldahl).
- II. 0.1648 gram substance gave 0.2496 gram AgCl.
0.4864 gram substance gave 0.0353 gram N.

	Calculated for $C_7H_5ONCl_2$	I	Found	II
Cl	37.32	37.52		37.44
N	7.37	7.12		7.27

Synthesis of 2-Chlortoluquinone

Action of Chlorine on 2-Nitrotoluene.—Janson¹ passed chlorine (1 molecule) into dry 2-nitrotoluene and reports the formation of a chlor compound melting at 37° and boiling at 236°–238°, to which he assigned the structure of 2-nitro-6-chlorotoluene. As necessary precautions Janson states that the nitro-

¹ Centralbl., 1900, I, 1110.

toluene must be pure and dry, that a chlorine carrier should be used, and that excess of chlorine must be avoided.

In accordance with these directions, 100 grams of pure dry 2-nitrotoluene, boiling at 218° , obtained by fractionating Kahlbaum's product, was mixed with 2 grams of iron filings dried at 115° , placed in a suitable vessel, and protected from moisture by a tube containing calcium chloride. Into this liquid the calculated amount of chlorine (obtained by the interaction of potassium permanganate and hydrochloric acid) was passed. The operation was begun with the liquid at the room temperature, but 30° – 40° was reached during the course of the reaction. When the liquid had cooled it was filtered from the excess of iron, made alkaline with a solution of sodium hydroxide and distilled with steam. The oil that came over was separated from water, dried over calcium chloride and cooled with ice and salt. No crystals¹ were obtained. The oil was next slowly fractionated, a Glinsky distilling tube being used, and the fraction boiling at 236° – 238° removed and cooled. Only a very small amount of solid separated.

When the above operation was carried out it was expected that chlorine might enter both ortho and para positions as respects methyl, and thus give rise to the isomers 2-nitro-6-chlortoluene and 2-nitro-4-chlortoluene. In order to prove that this had occurred, 30 grams of the oil (boiling at 236° – 238°) was reduced to the corresponding toluidine by means of tin and hydrochloric acid, after which the mixture was made alkaline and distilled with steam. The oil that came over was dried and fractionated and the portion obtained between 237° – 245° ² was next boiled for ten hours with glacial acetic acid and the mixture poured into 500 cc. water. The acetatoluide that separated was filtered off and fractionally crystallized as follows:

The entire mass was dissolved in boiling water and the liquid filtered through paper and allowed to come to the

¹ Janson states that at this point he was able to obtain crystals.

² 4-Chlor-2-toluidine boils at 237° (Goldschmidt and Honig: *Ber. d. chem. Ges.*, **19**, 2440 (1886)), and 6-chlor-2-toluidine boils at 245° (Wynne and Greeves: *Centralbl.*, **1896**, II, 530).

room temperature. The crystals that had formed were removed and further fractionated by treatment of their warm chloroform solution with one volume of ligroin (60° – 80°). Three crystallizations in this manner gave a fraction that melted sharply at 154° .¹ The aqueous filtrate that had been set aside meanwhile was now placed in the refrigerator and allowed to stand overnight. The solid that formed was removed and crystallized from hot water, and gave colorless needles that melted at 130° – 131° .² When these were dissolved in hot chloroform and the solution was mixed with enough ligroin (60° – 80°) to cause slight precipitation, warmed until solution occurred and then set aside to cool, the crystals that formed melted at 136° – 137° .

In order to determine whether this low-melting acettoluide is identical with Goldschmidt and Honig's³ product, some of the latter was prepared according to the directions given by these chemists, the start being made with pure 4-chlortoluene. When the acettoluide was crystallized once from water, it melted at 130° – 131° , as stated in the literature, but further crystallization from chloroform and ligroin, as specified above, raised the melting point to 136° – 137° , and a mixture of this product with the low-melting compound obtained from Janson's oil melted at the same temperature as either of them separately, which proves that they are identical. A mixture of either of these with the high-melting acettoluide, melting at 154° , softens at 110° , and is entirely melted at 123° . From this it follows that chlorination of 2-nitrotoluene gives both 4-chlor-2-nitrotoluene and 6-chlor-2-nitrotoluene.

Electrolytic Reduction of the Mixture of Chlornitrotoluenes.—Ten grams of the oil boiling at 236° – 238° , obtained by chlorinating *o*-nitrotoluene, was dissolved in 100 grams of sulphuric acid (1.84), and this solution diluted with 2 cc. water. Through this a current of 7.5 volts and 2.2 amperes was passed for ten hours, at the end of which time the liquid was poured into 360 cc. water and the mixture set aside to

¹ Wynne and Greeves (*loc. cit.*) and Janson (*loc. cit.*) found the melting point of the acettoluide from *o*-chlor-*o*-toluidine to be 157° – 159° .

² Goldschmidt and Honig: *Loc. cit.*

³ *Ibid.*

cool. It was next filtered, and the filtrate, which was deep purple in color, was cooled to about 0° , and 25 grams of powdered sodium dichromate was slowly added to oxidize the aminophenols produced to their corresponding quinones. The resulting mixture was allowed to come to room temperature during an hour, and was then distilled with steam. The yellow solid that passed over was dried and found to melt at 48° – 51° , which suggested a mixture of the *p*- and *o*-chlorotoluquinones, corresponding to the positions of chlorine already indicated by the acetoluides described.

A portion of this mixture was fractionated by crystallization from ligroin (40° – 60°), and there was obtained a fraction that separated in the form of yellow prisms melting at 105° , and was found to be identical with 4-chlorotoluquinone, a mixture of the two still melting at 105° . When mixed with 2-chlorotoluquinone, melting at 55° , the melting point was depressed exactly as stated on page 36. The combined mother liquors were allowed to evaporate, but the crystals obtained from them did not melt sharply, and repeated crystallization did not change this.

A second portion of the dried crude quinone, melting at 48° – 51° , mentioned above, was fractionally sublimed¹ at a temperature of 45° – 50° and a pressure of 15–17 mm. The process was very slow, and complete separation was not secured. The sublimate melted at 48° – 51° and behaved like 2-chlorotoluquinone containing a trace of the isomeric 4-chlorotoluquinone. The sublimate was next mixed with a little water, and saturation of this with sulphur dioxide gave a hydroquinone which, after one subsequent crystallization from water, melted at 173° and did not depress the melting point of 2-chlorotoluhydroquinone, melting at 173° , described on page 36. A mixture of this new product with 4-chlorotoluhydroquinone, melting at 176° , melts at 147° – 151° , showing that the new product is not identical with 4-chlorotoluhydroquinone.

A third portion of the dried crude quinone was reduced to hydroquinone, and gave crystals melting at 148° – 152° , indi-

Kempf: J. prakt. Chem., [2] 78, 203 (1909).

cating the presence of a mixture. This was dissolved in hot benzene,¹ the liquid filtered through cotton, the filtrate allowed to cool to the room temperature, and the crystals immediately removed. Recrystallization in this way three times and final crystallization from water gave a product melting at 174°-175°. A mixture of this with 2-chlortolhydroquinone, melting at 173°, melted at 173°-175°, while with 4-chlortolhydroquinone the melting point was depressed to 147°-151°.

It is thus clear that the mixture of 2-chlor-6-nitrotoluene and 4-chlor-6-nitrotoluene obtained by chlorinating *o*-nitrotoluene, whose structures were proved on the preceding pages, gives by electrolytic reduction and rearrangement in sulphuric acid solution the corresponding pair of aminophenols, viz., 1-methyl-2-chlor-6-aminophenol and 1-methyl-4-chlor-6-aminophenol, which in turn give by oxidation the two chlortoluquinones, viz., *p*-chlortoluquinone, melting at 105°, and *o*-chlortoluquinone, melting at 55°. The latter is identical with the chlortoluquinone, melting at 55°, obtained by oxidizing the chloraminocresol, melting at 166°-167°, produced by the action of chlorine on *p*-nitro-*m*-cresol, and subsequent reduction. It is thus shown that the chlorine atom enters into the ortho position to the methyl group in *p*-nitro-*m*-cresol and that it has that position in all the derivatives obtained from the chlorinated nitro-*m*-cresol, viz., the chloraminocresol, melting at 166°-167°,² and the chlorimido-chlortoluquinone, melting at 87°.

SUMMARY

The most important results of the work described in this paper may be summarized as follows:

1. (a) When *p*-nitro-*m*-cresol is chlorinated by passing chlorine, diluted with carbon dioxide, into a glacial acetic

¹ It had previously been noted that these two compounds differed in the rapidity with which crystals were deposited from benzene solution. 2-chlortolhydroquinone separating more quickly than its isomer.

² The work will be continued, and attempts made to isolate directly the chloraminocresols produced by the electrolytic reduction in sulphuric acid solution as described on page 39.

acid solution of the nitro compound, chlorine takes a position adjacent to methyl.¹

(b) *o*-Chlortoluquinone, the last of the three possible chlortoluquinones, was prepared by oxidation of the aminocresol obtained by reducing the chlorinated nitrocresol.

2. When *o*-nitrotoluene is chlorinated in the presence of iron, a mixture of the *o*- and the *p*-chlor-*o*-nitrotoluenes results.

3. When 2,4,6-tribrom-*m*-cresol is nitrated under certain conditions it gives rise to two isomeric mononitro derivatives, viz., 2,6-dibrom-4-nitro-*m*-cresol and 2,4-dibrom-6-nitro-*m*-cresol, while 2,4,6-trichlor-*m*-cresol could not be nitrated under any conditions employed in this work.

4. The chlorimidoquinones obtained as end products in these experiments do not appear to exist in stereoisomeric forms. Chlorimidochlortoluquinone was obtained in three forms, melting at 91°, 87°, and 65°, respectively, but they were proved to be structural isomers and not stereoisomers.

In conclusion, I hereby tender my sincere thanks to Professor Stieglitz for the painstaking scrutiny with which he has guided this work.

¹ Taking Kehrman's results, as well as my own, into consideration, one would be inclined to conclude that mixtures of this compound and its isomer, with the chlorine atom in a position para to the methyl group, are formed. In my work the formation of the ortho derivatives is conclusively proved.

